VAPOR PHASE DECOMPOSITION OF
AROMATIC HYDROCARBONS BY ELECTRIC DISCHARGE

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Introduction

Decomposition of organic compounds in presence of electric dis-
charge generally involves fragmentation and polymerization induced by
inelastic collision with high energy electrons. When hydrogen is
added, active hydrogen atoms produced by electric discharge also par-
ticipate in the decomposition reactions. The reaction mechanisms are
complex involving excited molecules, free radicals, and ions.

In this laboratory hydrocracking of coal, coal volatiles and re-
lated materials by electric discharge in hydrogen was studied. It is
postulated by Given[1] that coal (vitrinite) molecules contain aromatic
and hydroaromatic structures and probably fused aromatic ring nuclei
linked together by methylene or ethylene groups forming hydroaromatic
rings. Many of the replaceable hydrogens in the structure are sub-
stituted by hydroxyl or carbonyl groups. Short alkyl groups and
alicyclic rings may also be attached as side chains. In pyrolysis
at 500 - 600°C., dissociation of hydroxyl groups and dehydrogenation
of naphthenic rings take place. These acts lead to formation of OH
and H radicals which in turn help to break the linkages between aromatic
nuclei, forming smaller, partly aromatic volatile fragments, and at
the same time leaving a more aromatic residual structure behind.

On the other hand, high pressure hydrogenation of coal gives partial
or complete hydrogenation of the aromatic structure. When this is sub-
sequently cracked, the light products tend to be aliphatic rather than
aromatic hydrocarbons. It was thought that hydrocracking of coal by
electric discharge might be somewhere between pyrolysis and high pressure
hydrocracking. In the course of study it was thought important to test
this hypothesis by subjecting several aromatic or hydroaromatic compounds
to electric discharge in a hydrogen stream for better understanding of
the process. Organic compounds selected were m-cresol, ∝-methylnaphthalene
tetrahydronaphthalene, decahydronaphthalene, and 9, 10-dihydrophenanthrene

Experimental Apparatus and Procedures

The apparatus consisted of a vaporizer, a preheater, a discharge
reactor, and a product collecting system. The organic compound was fed
into the vaporizer at a certain rate and vaporized. Hydrogen was also

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[1] P. H. Given, presented Am. Chem. Soc., January, 1963 in
Cincinnati, Ohio

fed into the vaporizer at a certain flow rate and mixed with the organic vapor. The resultant mixture was then fed into the reactor through the preheater. The liquid products condensed in a water cooler were collected in a receiver and the gaseous products were collected in a liquid nitrogen trap. These products were analyzed by mass spectroscope and vapor phase chromatograph employing a 6 ft. column of 10% silicone rubber, SE-30 and 60-80 Chromosorb P.

The discharge reactor was fabricated with quartz and was of a concentric tube design similar to an ozonizer. The inside of the inner barrier (40 mm OD and 38 mm ID) and the outside of the outer barrier (48 mm OD and 46 mm ID) were coated with conductive, transparent, tin oxide. The former was connected to the high voltage terminal and the latter to ground. In this arrangement the electric discharge was sustained in an annular space, 46 mm OD, 40 mm ID, and 200 mm long. The inside barrier tube was filled with stainless steel wool and a thermometer was placed in the center. This thermometer and three thermistors attached to the outside electrode were used to determine the reactor temperature. The reactor was insulated with glass wool, and the reactor temperature was maintained at approximately 300°C. for all the runs.

The electric discharge power was supplied by feeding the output of a 10,000 Hertz, 30 kilowatt inductor-alternator to the primary of a 50 kilovolt transformer and, in turn, to a tuned circuit, to the reactor and to the high voltage instrumentation. The electric discharge power was determined by measuring the area of parallelogram on the oscilloscope[2].

When making the run, hydrogen was fed into the reactor at a definite flow rate and the electric discharge was applied to heat the reactor. When the reactor temperature was stabilized at about 300°C., the feed of the organic compound was started. The discharge power sustained for the reaction was in a range from 140 to 170 watts.

Experimental Results and Discussions

For cresol-hydrogen mixtures, two runs were made using the empty reactor and three runs were made by filling the reactor space with porous or activated aluminum oxide grains. For all the runs, the reactor pressure maintained at 300 mm Hg. Experimental results, including product distribution, are listed in Table 1. The principal products were phenol, toluene, benzene, aliphatic hydrocarbons, carbon dioxide and water. Among the aliphatic hydrocarbons, acetylene was present in the largest amount and about 80% was unsaturates except for Run 5. In this run the concentration of unsaturates was 55 %. This is probably due to a higher hydrogen concentration in the feed causing somewhat

[2] T. C. Manley, Trans. Am. Electro Chem. Soc. __84__ 83, 1943

more efficient hydrogenation. The bond energies of $C_6H_5-CH_3$ and C_6H_5-OH are 90 and 73 Kcal/mol. respectively. Despite this, it was observed that, in the products, phenol was in higher concentration than toluene.

Use of aluminum oxide packing in the discharge space was intended to investigate the possibility of increasing the energy yeild. Narrowing the gaseous discharge gap with dielectric packings may cause the following two effects on the discharge: (1) increase of discharge current for the same discharge power dissipated, and (2) increase of gaseous space breakdown field strength, if the gap decreases beyond a certain limit. The exact nature of the electric discharge employed in this study is still debatable.[3,4] However, it can be reasonably assumed that the primary reaction rate of the organic vapor with either high energy electrons or active hydrogen atoms may be dependent on discharge current density and field strength, if the system pressure and partial pressure of the reactant are constant. In electric discharge product of ozone. an increase in ozone concentration after filling the discharge gap with various dielectric packings is also reported by Morinaga and Suzuki.[5] In this study for approximately the same concentration of cresol vapor, the use of aluminum oxide grains in the discharge space appeared to increase the energy yield somewhat, but not conclusively.

In all the runs, the formation of brown solid films was observed on the reactor wall or on the surface of the grains. These solid films were not analyzed but they were insoluble in methylethyleketone or toluene. It is presumed that they are indicating possibly highly crosslinked polymerized products derived from the cresol. The energy yield for film formation was estimated to be in a range from 30 to 50 g/KWH; considerably higher than that for the fragmentation products.

Experimental results for the polycyclic compounds are summarized in Table 2. Methylnaphthalene vapor in hydrogen was tested under pressures of 760 and 74 mm Hg. The principal lighter products were aliphatic hydrocarbons, benzene and toluene. At the higher pressure the concentration of the lighter aliphatic hydrocarbons was in the order $C_2 > C_3 > C_4 > C_5$. At the lower pressure, however, this order was reversed. In both cases about 32 - 35% were unsaturates. The energy yield was approximately doubled by lowering the pressure.

For tetrahydronaphthalene, three experiments were made under different pressures. Among the lighter aliphatic hydrocarbons produced, the C_2 fraction was present in the largest amount, in which ethylene was in highest concentration followed by acetylene and ethane. The total percentage of unsaturates increased as the pressure decreased. This increase was essentially due to the increase in C_2 and C_3 unsaturates. As observed for methylnaphthalene, the energy yeild at 70 mm Hg was twice as high as that at 760 mm Hg. A considerably higher

[3] R. W. Lunt, Advanced Chem. Series, "Ozone Chemistry and Technology", Am. Chem. Soc., p. 286 (1959)

[4] M. Suzuki and Y. Naito, Proc. Japan Academy, 28 469 (1959)

[5] K. Morinaga and M. Suzuki, Bull. Chem. Soc., Japan 35 429 (1962)

energy yield than for the other two runs was observed at the intermediate pressure, 300 mm Hg.

When decahydronaphthalene was tested, one experiment was made under 760 mm Hg using 6.7% concentration in hydrogen. Another run was made under 300 mm Hg using 67% concentration. In the latter run, a higher energy yield was obtained. The product distribution was richer in the C_2 and C_3 fraction and also unsaturate concentration was higher.

One experiment was made to test dihydrophenanthrene in hydrogen. The gaseous products were essentially in the C_2 fraction; about 50% being unsaturated. Vapor phase chromatography of the liquid product showed two peaks. They were not identified but by the combined results of the VPC and mass spectroscope one of the peaks was tentatively identified as butylbenzene. Biphenyl, which is a likely decomposition product, was not found. For the polycyclic aromatic and hydroaromatic compounds tested in this study, the energy yield from electric discharge hydrocarcking for production of the lighter hydrocarbons was in the following order:
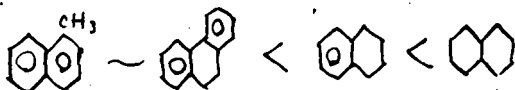
As observed in cresol runs, solid films were formed on the reactor wall, but they were not analyzed.

The number of experiments are not sufficient to permit drawing a concrete relationship between energy yield and molecular structure. The resonance energies of benzene, naphthalene, and phenenthrene are 39, 75, and 110 Kcal, respectively. It is reasonable to assume that the condensed aromatic ring structure absorbs large amounts of energy and requires high energy for cracking. The radiation effect on various polycyclic aromatic compounds were studied by Weiss et al[6]. They discussed correlations between the radiation stability and various structural factors. These include resonance energy, electron affinity, and ionization constant. Since there is a close similarity between radiation and electric discharge in principle, further information along this line would be helpful for a better understanding of the electric discharge hydrocracking process.

Elucidation of the reaction scheme in detail is beyond the scope of the this study. However, it was indicated that in electric discharge hydrocracking of aromatic or hydroaromatic hydrocarbons, dissociation of the side chains and rupture of the rings are followed by secondary reactions involving the decomposed species; this leads to the formation of aromatic or aliphatic lighter compounds. Energy requirement to form these lighter compounds appear to be too high for practical applications. The formation of the solid polymerized products, which takes

[6] J. Weiss, C. H. Collins, J. Sucker, and N. Carciello, Ind. Eng. Chem, Prod. Res. and Development, 3, 73 (1964)

place in parallel with fragmentation, as seen for cresol runs, requires considerably less energy. Study on the formation of polymer films starting with various monomers and using the present discharge system presents an extremely interesting problem which is currently under investigation.

Table 1

Exp. No.	m-cresol Conc. %	Reactor Packings	Organic Products Distributions, g/KWH				Energy Yield g/KWH	Unsaturates in Aliphatic %
			Aromatic H/C C_6	C_7	Aliphatic H/C	Phenol		
1	88.8	no	0.8	2.7	1.4	4.3	9.2	78
2	65.5	no	0.5	2.3	1.0	3.2	7.0	85
3	93.0	porous alumina	1.0	4.1	2.2	4.4	11.7	82
4	35.5	porous alumina	0.8	2.1	1.5	3.1	7.5	55
5	67.5	activated alumina	0.2	0.9	1.4	6.8	9.3	80

Electric Discharge Hydrocracking of m-cresol

Table 2

Exp. No.	Organic Vapor	Vapor Conc. %	Pressure mmHg	Energy Yield g/KWH	Product Distribution, Wt.%						
					C_1	C_2	C_3	C_4	C_5	C_6-C_9	Unsaturated
6		4.5	760	0.66	2	33	24	21	13	7	32
7		5.8	74	1.2	8	5	24	29	40	2	35
8		5.8	760	1.5	5	77	12	3	1	2	74
9		7.3	300	8.8	1	78	16	3	1	2	85
10		7.4	70	3.0	--	74	23	2	.5	.5	90
11		6.7	760	3.9	4	38	20	10	7	21	49
12		66.7	300	5.4	4	56	27	7	2	7	76
13*		4.5	760	0.69	3	23	7	3	2	1	71**

* The balance of the product distribution for this run (60%) was the heavier fractions which were not identified by VPC.

** Percentage of unsaturates in C_1-C_9 fractions

Hydrocracking of Polycylic Aromatic and Hydroaromatic Compounds